

PATENT SPECIFICATION

(11) 1364 199

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- (21) Application No. 54097/72 (22) Filed 22 Nov. 1972
 (31) Convention Application No. P 21 59 991.7
 (32) Filed 3 Dec. 1971 in
 (33) Germany (DT)
 (44) Complete Specification published 21 Aug. 1974
 (51) International Classification C07F 7/18
 (52) Index at acceptance

C3S 2 7B 7D P2A

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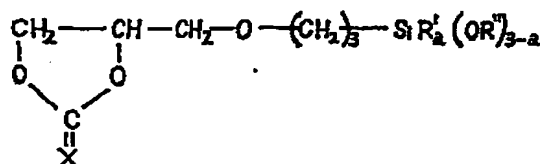
(54) SILICON-CONTAINING DIOXOLANE DERIVATIVES

(71) We, DYNAMIT NOBEL AKTIENGESELLSCHAFT, a German company, of 521 Troisdorf, near Cologne, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

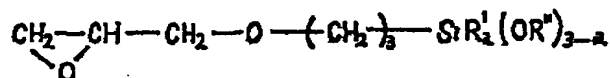
This invention relates to silicon-containing dioxolane derivatives and their use in the preparation of organosilane esters containing an epoxy group.

Organosilanes containing an epoxy group have been commercially used for a number of different purposes. For example, they are used as adhesives for bonding organic polymers, such as epoxide resins or phenolic resins, to glass fibres, mats or rovings, and for improving adhesion in the binding of sand casting moulds. Successful attempts have also been made to improve the adhesion between plastics and metals by using organosilanes of this kind.

In accordance with the invention, it has been found that hitherto unknown silicon-containing dioxolane derivatives can be used as starting materials in the preparation of such organosilane esters. These silicon-containing dioxolane derivatives are compounds having the general formula:

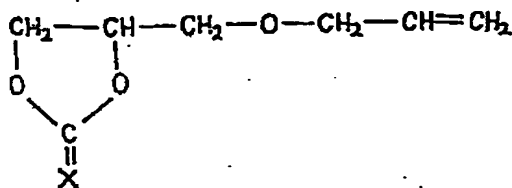


in which a is 0 or 1, X is a single oxygen atom or two hydrogen atoms, and R' and R'' are the same or different and are each an alkyl group. Such silicon-containing dioxolane derivatives can be used to prepare an organosilane ester having the general formula:



in which a , R' and R'' are as defined above, by the process which comprises heating the dioxolane derivative, resulting in the liberation of carbon dioxide (when X is a single oxygen atom) or formaldehyde (when X is two hydrogen atoms).

The silicon-containing dioxolane derivatives can be prepared by the process which comprises reacting a compound having the general formula:



in which X is as defined above, with a silane having the general formula:



in which a, R' and R'' are as defined above, in the presence of a platinum compound.

In the general formulae given above, R' and R'' are preferably alkyl groups containing from 1 to 4 carbon atoms.

The process in which the silicon containing dioxolane derivatives are heated is preferably carried out under normal pressure *in vacuo*. When it is carried out under normal pressure, carbon dioxide or formaldehyde can be liberated at temperatures of from 130 to 240°C, preferably at temperatures of from 140 to 180°C. Some liberation also takes place at lower temperatures, especially when catalysts, such as calcium oxide for example, are present. The liberation of carbon dioxide or formaldehyde can also be carried out at lower temperatures when the process is carried out *in vacuo*. In this case, it is of advantage to heat the derivative to its boiling point at the particular reduced pressure. Since the organosilane ester formed has a lower boiling point than the dioxolane derivative, this procedure has the advantage that the required organosilane ester can be directly separated off from the reaction zone by use of a reflux column.

In another preferred embodiment of the preparation of the organosilane ester, liberation is carried out in the presence of a compound which binds the carbon dioxide or the formaldehyde liberated without reacting either with the dioxolane derivative or with the organosilane ester. Examples of such compounds are alkaline earth metals oxides (for example calcium oxide) or other basic metal oxides (for example zinc oxide), and alkaline earth metal carbonates. These compounds are preferably used in stoichiometric quantities with respect to the dioxolane derivative.

As noted above, the silicon-containing dioxolane derivatives can be prepared by the chemical addition of 4-allyloxymethyl-2-oxo-1,3-dioxolane or 4-allyloxymethyl-1,3-dioxolane to a di- or tri-alkoxy hydrogen silane in the presence of a platinum compound as a catalyst. The addition can take place at a temperature as low as about 70°C. The reaction is preferably carried out in a solvent which is inert to the dioxolane, the dioxolane derivative and the silane.

Examples of dioxolane derivatives within the above general formulae are 4-(3-trimethoxysilylpropoxymethyl)-2-oxo-1,3-dioxolane and 4-(3-trimethoxysilylpropoxymethyl)-1,3-dioxolane, both of which form 3-glycidyloxypropyl trimethoxysilane upon heating, the first through the elimination of carbon dioxide and the second through the liberation of formaldehyde.

The invention will now be illustrated by the following Examples.

EXAMPLE 1

840 g of 4-(3'-trimethoxysilylpropoxymethyl)-2-oxo-1,3-dioxolane were boiled vigorously with 170 g of dry calcium oxide at 5 Torr in a 12-plate vacuum distillation column containing a multifil filling with a gap volume of 96%. There were obtained 701 g of a distillate having a boiling point of 124—126°C (5 Torr), a refractive index $[n_D^{20}]$ of 1.4278, and a density $[D_4^{20}]$ of 1.070 over a period of three hours at a reflux ratio of 8. The distillate was substantially pure 3-glycidyloxypropyl trimethoxysilane, its refractive index, density and IR-spectrum being identical to those of a specimen known to be 3-glycidyloxypropyl trimethoxysilane.

EXAMPLE 2

The following reaction was carried out in a 4-litre multi-necked flask equipped with a flat paddle mixer, two dropping funnels, an internal thermometer and a reflux condenser, under an atmosphere of nitrogen.

0.5 ml of a 1/100 molar solution of chloroplatinic acid in acetone was stirred into 316 g of 4-allyloxymethyl-2-oxo-1,3-dioxolane in the flask, and the resulting mixture heated to 70°C. The heat was removed and the reaction carried out over a period of

three hours by the simultaneous dropwise addition of 1464 g of trimethoxysilane and 1580 g of 4-allyloxymethyl-2-oxo-1,3-dioxolane, at a reaction temperature kept at 70°C by external cooling. This was followed by stirring for 1 hour at 70°C. The colourless to pale yellow reaction product consisted of 4-(3'-trimethoxysilylpropoxymethyl)-2-oxo-1,3-dioxolane. Distillation *in vacuo* gave a yield of 3344 g. The distillate had a boiling point of 155°C (2 Torr), a refractive index [n_D^{25}] of 1.4389, and a density [D_4^{20}] of 1.184. The product formed a clear solution in water. Elemental analysis for $C_{10}H_{20}O_7Si$ (MW=280) gave the following results:

	C(%)	H(%)	O(%)	Si(%)
calculated:	42.8	7.14	30.06	10.0
found:	42.9	7.3	29.6	10.2

The IR-spectrum showed a strong carbonyl band at 1799 cm^{-1} due to the C=O group on the dioxolane ring.

EXAMPLE 3

A reaction was carried out as in Example 2 by initially introducing 288 g of 4-allyloxymethyl-1,3-dioxolane together with 0.5 ml of catalyst into the flask, and simultaneously adding dropwise 1464 g of trimethoxysilane and 1440 g of 4-allyloxymethyl-1,3-dioxolane at a temperature of 70°C.

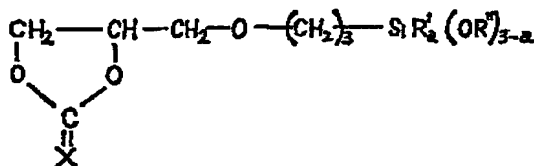
The colourless to pale yellow crude product was 4-(3'-trimethoxysilylpropoxymethyl)-1,3-dioxolane. Distillation *in vacuo* gave a yield of 3179 g. The product had a boiling point of 128°C (2 Torr) a refractive index [n_D^{25}] of 1.4362, and a density [D_4^{20}] of 1.062. The product formed a clear solution in water.

Elemental analysis for $C_{10}H_{20}O_6Si$ (MW=266) gave the following results:

	C(%)	H(%)	Si(%)
calculated:	45.1	8.27	10.5
found:	45.3	8.4	10.4

WHAT WE CLAIM IS:—

1. A silicon-containing dioxolane derivative having the general formula:



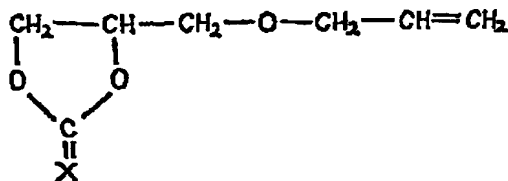
in which a is 0 or 1; X is a single oxygen atom or two hydrogen atoms, and R' and R'' are the same or different and are each an alkyl group.

2. A dioxolane derivative as claimed in claim 1, in which R' and R'' are each an alkyl group containing from 1 to 4 carbon atoms.

3. 4-(3'-Trimethoxysilylpropoxymethyl)-2-oxo-1,3-dioxolane.

4. 4-(3'-Trimethoxysilylpropoxymethyl)-1,3-dioxolane.

5. A process for the preparation of a silicon-containing dioxolane derivative as claimed in claim 1, which comprises reacting a compound having the general formula:



in which X is as defined in claim 1, with a silane having the general formula:



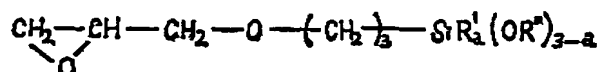
in which a , R' and R'' are as defined in claim 1, in the presence of a platinum compound.

6. A process according to claim 5, in which the reaction is carried out in a solvent which is inert to the reactants and the reaction product.

7. A process for the preparation of a silicon-containing dioxolane derivative, substantially as described in the foregoing Example 2 or Example 3.

5 8. A silicon-containing dioxolane derivative whenever obtained by the process claimed in any one of claims 5 to 7. 5

9. A process for the preparation of an organosilane ester having the general formula:



10 in which a, R' and R'' are as defined in claim 1, which comprises heating a silicon-containing dioxolane derivative as claimed in any one of claims 1 to 4 and 8. 10

10. A process according to claim 9, in which the silicon-containing dioxolane derivative is heated at a temperature of from 130 to 240°C.

11. A process according to claim 10, in which the silicon-containing dioxolane derivative is heated at a temperature of from 140 to 180°C. 15

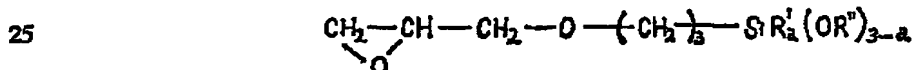
12. A process according to claim 9, 10 or 11, in which the silicon-containing dioxolane derivative is heated *in vacuo*.

13. A process according to any one of claims 9 to 12, in which the silicon-containing dioxolane derivative is heated in the presence of a compound which binds the carbon dioxide or formaldehyde liberated by heating. 20

14. A process according to claim 13, in which the compound is calcium oxide.

15. A process for the preparation of an organosilane ester, substantially as described in the foregoing Example 1.

16. An organosilane ester having the general formula:



in which a, R' and R'' are as defined in claim 1, whenever obtained by the process claimed in any one of claims 9 to 15.

17. An organosilane ester as claimed in claim 16, in which R' and R'' are each an alkyl group containing from 1 to 4 carbon atoms. 30

18. An organosilane ester as claimed in claim 17, the ester being 3-glycidyloxypropyl trimethoxysilane. 30

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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